Syntheses of Some Hydrotris(3,5-dimethylpyrazol-1-yl)-borato(aryloxo)zirconium(IV) Complexes and the X-Ray Crystal Structures of $[ZrL(OC_6H_4NO_2\text{-}4)_3]$, $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$ and $[ZrL(Cl)(OC_6H_3Me_2\text{-}2,6)_2]$ ($L = 3,5\text{-}Me_2C_3N_2H$)‡

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The compound $[ZrLCl_3]$ [$L = HB(3,5\text{-}Me_2C_3N_2H)_3$] reacts with the sterically undemanding phenol derivatives HOC_6H_4Z (Z = H, 2-F, 3-F, 4-F, 3-NO_2, 4-NO_2 or 4-Bu^t) to give only the tris(aryloxo) complexes $[ZrL(OC_6H_4Z)_3]$, even when $[ZrLCl_3]$ is present in excess. When sterically demanding phenol derivatives are used it is possible to obtain mixed chloro–aryloxo zirconium complexes so that $[ZrL(Cl)(OC_6H_3Me_2\text{-}2,6)_2]$, $[ZrL(Cl)(OC_6H_4Ph\text{-}2)_2]$, $[ZrLCl_2(OC_6H_3Me_2\text{-}2,6)]$ and $[ZrLCl_2(OC_6H_3Ph_2\text{-}2,6)]$ have been isolated in addition to $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$ and $[ZrL(OC_6H_4Ph\text{-}2)_3]$. X-Ray crystallographic studies of $[ZrL(OC_6H_4NO_2\text{-}4)_3]$, $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$ and $[ZrL(Cl)(OC_6H_3Me_2\text{-}2,6)_2]$ reveal that, in each case, the zirconium ion has a distorted-octahedral co-ordination geometry. The respective Zr–O(aryl) distances for these complexes are 1.978(1), 1.973(3) (mean) and 1.948(1) Å (mean); while the respective Zr–O–C(aryl) angles are 161.4(1), 175(1) (mean) and 174(2)° (mean). In all of these structures the aryl group is found to be oriented towards the ligand L and interposed between neighbouring $3,5\text{-}Me_2C_3N_2H$ moieties.

The tripodal ligand hydrotris(pyrazol-1-yl)borate, $HB(pz)_3$, has been considered as a formal analogue of cyclopentadienide, being a uninegative three-electron-pair ligand which occupies three co-ordination sites on a metal. Accordingly $HB(pz)_3$ forms many complexes which have counterparts containing the cyclopentadienide ligand.[1] However, despite this formal similarity there are significant steric[2–4] and electronic[5] differences between $HB(pz)_3$ and $\eta^5\text{-}C_5H_5$. The structural differences between $HB(pz)_3$ and $\eta^5\text{-}C_5H_5$ may be further amplified if substituents are present in the 3 positions of the pyrazolyl rings. These substituents project across the metal co-ordination sphere towards the trigonal-prismatic co-ordination sites inhibiting the binding of more than three co-ligands. Thus $HB(3,5\text{-}Me_2C_3N_2H)_3$, L, usually favours a co-ordination number of six, even with the early d-block metals where higher co-ordination numbers might normally be preferred.[6] One exception to this generalisation is provided by $[TaL(Me)Cl_3]$ which is seven-co-ordinate.[7] In the case of zirconium the nominally eight-co-ordinate complexes $[Zr(\eta^5\text{-}C_5H_5)\{HB(pz)_3\}X_2]$ (X = Cl or OC_6H_4Z; Z = H, 4-OMe, 4-NO_2, or 2-Ph) can be obtained with $HB(pz)_3$.[8,9] The currently known complexes of Zr with L are derived from $[ZrLCl_3]$[10] and are, in the main, six-co-ordinate. Thus some alkoxy derivatives of this sterically constrained complex have been reported. These include $[ZrLCl_2(OMe)]$,[10] $[ZrLCl_2(OBu^t)]$[11] and $[ZrL(Cl)(OBu^t)_2]$.[12] Some organometallic derivatives have also been obtained and $[ZrL(OBu^t)Me_2]$ reacts with $C{\equiv}NCMe_3$ to give $[ZrL(OBu^t)Me(\eta^2\text{-}MeC{=}NCMe_3)]$[12] which is seven-co-ordinate and contains an η^2 ligand occupying a notionally octahedral site. The ability of L to accommodate two OBu^t ligands when bound to Zr^{IV} suggests that quite sterically bulky co-ligands can be tolerated by L in its complexes with Zr^{IV}. In order further to investigate the ability of the ZrL moiety to tolerate sterically demanding co-ligands, we have examined the syntheses and structures of some aryloxo derivatives of $[ZrLCl_3]$ containing both sterically undemanding[13] and sterically demanding ligands. The use of steric bulk to determine the extent of chloride substitution in $[ZrLCl_3]$ has also been investigated. The crystal structure of $[ZrL(OC_6H_4NO_2\text{-}4)_3]$ has been reported[13] in preliminary form.

Discussion

Synthetic Studies.—The reactions of $[ZrLCl_3]$ with 3 equivalents of HOC_6H_4Z (Z = H, 3-NO_2, 4-NO_2, 2-F, 3-F, 4-F, or 4-Bu^t) in dichloromethane containing triethylamine afforded the air-stable tris(phenoxide) complexes $[ZrL(OC_6H_4Z)_3]$ in yields ranging from 51 to 88%. When 2 equivalents of HOC_6H_4Z (Z = H or 4-NO_2) were used in an attempt to substitute just two of the chloride ligands only $[ZrL(OC_6H_4Z)_3]$ could be isolated. When these reactions were carried out using a 1:1 $[ZrLCl_3]$:HOC_6H_4Z stoichiometry, unreacted $[ZrLCl_3]$ and a mixture of two or more components, not including $[ZrL(OC_6H_4Z)_3]$, could be detected by ^1H NMR spectroscopy. However, we were unable to isolate mono-or bis-phenoxide derivatives from these reactions. The reaction between $[ZrLCl_3]$ and $HOC_6H_4NO_2\text{-}2$ did not afford any tractable products. A reaction involving a 1:1:2 molar ratio of $[ZrLCl_3]$, $HOC_6H_4NO_2\text{-}2$ and HOPh afforded only $[ZrL(OPh)_3]$.

The reaction between $[ZrLCl_3]$ and 1 equivalent of 2-phenylphenol in the absence of a base affforded $[ZrL(Cl)(OC_6H_4Ph\text{-}2)_2]$ rather than the expected monosubstituted complex. Furthermore, despite the sterically bulky nature of $HOC_6H_4Ph\text{-}2$, it was possible to obtain $[ZrL(OC_6H_4Ph\text{-}2)_3]$ from the reaction of $[ZrLCl_3]$ with 3 equivalents of 2-phenylphenol in the presence of triethylamine. Proton NMR studies of

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‡ [Hydrotris(pyrazol-1-yl-κN^2)borato]-tris(4-nitrophenoxo)-zirconium(IV), -tris(2,6-dimethylphenoxo)zirconium(IV) and -chlorobis-(2,6-dimethylphenoxo)zirconium(IV).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses for $[ZrL(OC_6H_4NO_2\text{-}4)_3]$ **1**

Atom	*x*	*y*	*z*
Zr*	15 636(2)	15 636(2)	15 636(2)
B	3 307(2)	3 307(2)	3 307(2)
N(1)	3 405(1)	1 554(1)	2 101(1)
N(2)	3 937(1)	2 357(1)	2 826(1)
N(3)	1 262(2)	−3 819(2)	4 118(2)
O(1)	1 342(1)	3(1)	1 889(1)
O(2)	1 779(2)	−3 801(2)	5 002(2)
O(3)	698(2)	−4 616(2)	3 711(2)
C(1)	3 879(2)	−159(2)	1 076(2)
C(2)	4 161(2)	854(2)	1 821(2)
C(3)	5 166(2)	1 210(2)	2 358(2)
C(4)	5 004(2)	2 155(2)	2 984(2)
C(5)	5 802(2)	2 867(2)	3 751(2)
C(6)	1 356(2)	−921(2)	2 420(2)
C(7)	2 030(2)	−972(2)	3 375(2)
C(8)	2 004(2)	−1 925(2)	3 928(2)
C(9)	1 309(2)	−2 816(2)	3 511(2)
C(10)	653(2)	−2 788(2)	2 558(2)
C(11)	670(2)	−1 838(2)	2 011(2)

* Fractional coordinates $\times 10^5$.

the reaction revealed no evidence for the presence of monophenoxide derivatives or $[ZrLCl_3]$ in the product mixture. A further increase in the steric bulk of the aryloxo ligand was obtained by using $HOC_6H_3Me_2\text{-}2,6$ and in this case, depending on the reaction conditions, the complete series $[ZrL(Cl)(OC_6H_3Me_2\text{-}2,6)_2]$, $[ZrLCl_2(OC_6H_3Me_2\text{-}2,6)]$ or $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$ could be isolated. However, satisfactory elemental analyses could not be obtained for $[ZrL(Cl)(OC_6H_3Me_2\text{-}2,6)_2]$ and this complex was identified on the basis of spectroscopic measurements only. The monoaryloxo complex was obtained by heating $[ZrLCl_3]$ with 2 equivalents of $HOC_6H_3Me_2\text{-}2,6$ in toluene under reflux overnight, the bis(aryloxo) complex by heating $[ZrLCl_3]$ with 3 equivalents of $HOC_6H_3Me_2\text{-}2,6$ in xylene under reflux for 1 week, and the tris(aryloxo) complex was obtained *immediately* on treating $[ZrLCl_3]$ with 3 equivalents of $HOC_6H_3Me_2\text{-}2,6$ in dichloromethane containing an excess of triethylamine. This finding dramatically demonstrates the effect of a base on the substitution reactions with this bulky phenol derivative. In the absence of a base the tris(aryloxo) complex did not form, even under reflux in high-boiling solvents such as xylene or diglyme (2,5,8-trioxanonane), over a period of 1 week.

Only the reactants could be recovered from the reaction between $[ZrLCl_3]$ and 1 equivalent each of 2,6-diphenylphenol and NEt_3. However, when the reaction was repeated using 3 equivalents each of $HOC_6H_3Ph_2\text{-}2,6$ and NEt_3 the monophenoxide derivative $[ZrLCl_2(OC_6H_3Ph_2\text{-}2,6)]$ was obtained. This compound was isolated as a solvate containing varying amounts of CH_2Cl_2 which could not be completely removed by drying *in vacuo* as shown by elemental analyses and ^1H NMR measurements. It is necessary to carry out this reaction under rigorously anhydrous conditions. The presence of moisture leads to the formation of another product tentatively formulated as $[ZrL(Cl)(OH)(OC_6H_3Ph_2\text{-}2,6)]$ on the basis of ^1H NMR and mass spectral data. The reaction between $[ZrLCl_3]$ and 2,6-di(*tert*-butyl)phenol was also investigated. Zirconium phenoxide derivatives could not be isolated from reactions with an excess of this ligand in the presence of NEt_3 or metallic sodium.

Attempts were made to synthesise organometallic compounds by treating the chlorophenoxide derivatives with methyllithium: $[ZrL(Cl)(OC_6H_4Ph\text{-}2)_2]$ and $[ZrLCl_2(OC_6H_3Me_2\text{-}2,6)]$ were treated respectively with 1 and 2 equivalents of LiMe and the reactions were monitored by ^1H NMR spectroscopy. In the case of $[ZrL(Cl)(OC_6H_4Ph\text{-}2)_2]$ the only product which could be identified was $[ZrL(OC_6H_4Ph\text{-}2)_3]$. However, in the reaction with $[ZrLCl_2(OC_6H_3Me_2\text{-}2,6)]$ no identifiable products were obtained and the zirconium complex appeared to have been destroyed. When $[ZrLCl_2(OC_6H_3Ph_2\text{-}2,6)]$ was treated with 1 equivalent of LiMe unreacted $[ZrLCl_2(OC_6H_3Ph_2\text{-}2,6)]$ could be identified in the reaction mixture and there was no evidence for the formation of methyl complexes. The reaction between $[ZrL(Cl)(OC_6H_4Ph\text{-}2)_2]$ and vinylmagnesium bromide was also attempted but again only the reagents could be observed by ^1H NMR spectroscopy and no reaction was evident.

The ^1H NMR spectra of the tris(phenoxide) derivatives $[ZrL(OC_6H_4Z)_3]$ (Z = H, 2-F, 3-F, 4-F, 3-NO_2, 4-NO_2 or 4-Bu^t), $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$ and $[ZrL(OC_6H_4Ph\text{-}2)_3]$ contain two singlets each of relative area 9 in the region δ 1.2–2.6 attributable to the pyrazolyl methyl groups in a complex with C_{3v} point symmetry. The pyrazolyl H^4 proton appears as a singlet of relative area 3 in the region δ 5.7–5.8. The aryl protons appear in the region δ 6.1–8.1 and, in the case of the complexes containing 4-substituted phenoxide ligands, only two proton environments are apparent. Thus both edges of the phenyl ring are equivalent showing that rotation of the phenyl ring about the C–O bond is rapid on the NMR time-scale. In $[ZrL(OC_6H_4NO_2\text{-}4)_3]$ this equivalence persists down to −95 °C. In $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$ the 2- and 6-methyl substituents on the aryl rings give rise to distinct signals indicating that there is not free rotation about the C–O bond in this complex.

The ^1H NMR spectra of the bis(phenoxide) derivatives $[ZrL(Cl)(OC_6H_4Ph\text{-}2)_2]$ and $[ZrL(Cl)(OC_6H_3Me_2\text{-}2,6)_2]$ and of the monophenoxide derivatives $[ZrLCl_2(OC_6H_3Me_2\text{-}2,6)]$ and $[ZrLCl_2(OC_6H_3Ph_2\text{-}2,6)]$ are consistent with the presence of a plane of symmetry in the molecule. Thus the spectra of $[ZrL(Cl)(OC_6H_4Ph\text{-}2)_2]$ and $[ZrLCl_2(OC_6H_3Ph_2\text{-}2,6)]$ contain two singlets of relative areas 2:1 in the region δ 5.4–5.7 attributable to the pyrazolyl H^4 signals. The pyrazolyl methyl signals appear as four singlets of relative areas 6:6:3:3 in the regions δ 1.6–2.6, again in accord with the presence of a plane of symmetry. The spectrum of $[ZrL(Cl)(OC_6H_3Me_2\text{-}2,6)_2]$ contains six singlets in the area ratios 6:3:6:6:3:6 in the region δ 1.2–2.8 arising from two pairs of equivalent aryl-methyl groups, two pairs of equivalent pyrazolyl-methyl groups and two unique pyrazolyl-methyl groups. The pyrazolyl H^4 protons appear as a single resonance of relative area 3 in this case. The spectrum of $[ZrLCl_2(OC_6H_3Me_2\text{-}2,6)]$ contains five singlets of relative areas 3:6:9:3:3 in the region δ 1.4–2.8 attributable to two pairs of equivalent pyrazolyl-methyl groups, two unique pyrazolyl-methyl groups and two unique aryl-methyl groups. In this case the pyrazolyl H^4 protons give rise to two singlets at δ 5.77 and 5.86 and of relative areas 2:1.

The IR spectra of the new complexes are unremarkable and all contain bands attributable to the presence of L, including ν_{BH} at *ca.* 2550 cm^{-1}, and to the aryl group of the phenoxide ligand. All of the complexes exhibit molecular ions in their mass spectra, along with an ion at *m*/*z* 375 attributable to $[Zr(3,5\text{-}Me_2C_3N_2H)_3]^+$, in addition to other fragment ions.

*Structural Studies.**—In order to obtain more detailed structural information about the steric interactions between L and the 2 substituents of the aryl rings in these compounds, single-crystal X-ray diffraction studies were carried out on $[ZrL(OC_6H_4NO_2\text{-}4)_3]$,[13] $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$ and $[ZrL(Cl)(OC_6H_3Me_2\text{-}2,6)_2]$. These compounds provide examples of a complex containing three sterically undemanding phenoxide ligands, a complex containing three sterically demanding phenoxide ligands and a complex containing one chloride and two sterically demanding phenoxide ligands. Attempts to grow

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* Contribution from the Crystallography Unit, Universities of Aston and Birmingham.

Table 2 Fractional atomic coordinates (× 10^4) with e.s.d.s in parentheses for $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$ **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Zr*	0	13 916(3)	0	C(22)	1 862(3)	−1 174(7)	2 300(5)
O(1)	537(2)	2 485(4)	−478(2)	C(23)	1 364(3)	−791(5)	1 638(3)
C(1)	920(3)	3 171(6)	−813(3)	C(24)	1 035(4)	−1 743(6)	1 045(4)
C(2)	1 478(3)	3 864(6)	−365(4)	N(1)	−654(2)	−207(4)	305(2)
C(3)	1 680(4)	3 769(8)	483(4)	N(2)	−1 015(2)	−1 080(3)	−214(2)
C(4)	1 855(3)	4 591(6)	−711(5)	C(25)	−1 361(3)	−1 858(5)	114(3)
C(5)	1 699(4)	4 650(7)	−1 481(5)	C(26)	−1 793(3)	−2 920(6)	−296(4)
C(6)	1 168(4)	3 925(6)	−1 920(4)	C(27)	−1 228(3)	−1 489(5)	853(3)
C(7)	778(3)	3 142(5)	−1 593(3)	C(28)	−794(3)	−450(5)	960(3)
C(8)	254(3)	2 279(7)	−2 068(3)	C(29)	−503(3)	313(5)	1 651(3)
O(2)	−523(2)	2 663(3)	384(2)	N(3)	296(2)	−290(4)	−655(2)
C(9)	−887(3)	3 429(5)	703(4)	N(4)	−172(2)	−1 227(3)	−979(3)
C(10)	−1 552(3)	3 105(5)	724(3)	C(30)	157(3)	−2 156(5)	−1 223(3)
C(11)	−1 930(3)	2 003(6)	308(4)	C(31)	−181(4)	−3 331(6)	−1 571(6)
C(12)	−1 886(4)	3 846(7)	1 131(4)	C(32)	852(3)	−1 819(6)	−1 049(4)
C(13)	−1 561(5)	4 924(9)	1 491(5)	C(33)	906(3)	−662(6)	−711(3)
C(14)	−942(5)	5 279(7)	1 422(4)	C(34)	1 549(3)	127(5)	−416(4)
C(15)	−594(3)	4 558(5)	1 034(4)	N(5)	−947(2)	1 288(4)	−1 076(3)
C(16)	82(4)	5 010(6)	898(6)	N(6)	−1 207(2)	165(4)	−1 411(3)
O(3)	720(2)	900(3)	920(2)	C(35)	−1 695(2)	410(5)	−2 067(3)
C(17)	1 180(3)	476(5)	1 558(3)	C(36)	−2 070(4)	−625(7)	−2 571(4)
C(18)	1 444(3)	1 317(6)	2 158(3)	C(37)	−1 756(3)	1 683(5)	−2 153(3)
C(19)	1 190(4)	2 642(5)	2 097(3)	C(38)	−1 289(2)	2 213(5)	−1 535(3)
C(20)	1 938(3)	910(7)	2 796(3)	C(39)	−1 142(3)	3 564(5)	−1 345(4)
C(21)	2 148(4)	−317(8)	2 857(5)	B	−939(3)	−1 084(6)	−1 029(4)

* Fractional coordinates × 10^5.

Table 3 Fractional atomic coordinates (× 10^4) with e.s.d.s in parentheses for $[ZrL(Cl)(OC_6H_3Me_2\text{-}2,6)_2]$ **3**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Zr*	40 000(2)	34 569(5)	10 927(2)	N(2)	2 839(2)	2 081(4)	754(1)
Cl	4 124(1)	5 205(1)	485(1)	C(17)	2 302(2)	2 256(6)	648(2)
O(1)	4 760(1)	2 958(4)	1 230(1)	C(18)	1 919(2)	1 152(6)	527(2)
C(1)	5 279(2)	2 479(6)	1 280(2)	C(19)	2 192(2)	3 573(6)	671(2)
C(2)	5 715(2)	3 370(8)	1 275(2)	C(20)	2 684(2)	4 199(5)	793(2)
C(3)	5 609(3)	4 812(8)	1 176(3)	C(21)	2 794(2)	5 634(6)	860(3)
C(4)	6 242(3)	2 885(11)	1 345(3)	N(3)	4 003(2)	1 886(4)	458(1)
C(5)	6 342(3)	1 573(11)	1 410(3)	N(4)	3 658(2)	819(4)	469(1)
C(6)	5 914(3)	704(8)	1 404(2)	C(22)	3 816(2)	−96(5)	141(2)
C(7)	5 371(2)	1 146(7)	1 335(2)	C(23)	3 538(3)	−1 391(6)	69(2)
C(8)	4 911(3)	137(6)	1 331(3)	C(24)	4 268(2)	402(6)	−96(2)
O(2)	3 817(1)	4 585(3)	1 650(1)	C(25)	4 371(2)	1 623(6)	111(2)
C(9)	3 686(2)	5 305(5)	2 050(2)	C(26)	4 816(2)	2 549(6)	−16(2)
C(10)	3 207(2)	5 065(6)	2 305(2)	N(5)	3 724(2)	1 700(4)	1 553(1)
C(11)	2 827(3)	3 972(7)	2 140(3)	N(6)	3 389(2)	716(4)	1 364(1)
C(12)	3 106(3)	5 833(7)	2 718(2)	C(27)	3 313(2)	−190(5)	1 720(2)
C(13)	3 458(3)	6 801(7)	2 878(2)	C(28)	2 988(3)	−1 422(5)	1 618(2)
C(14)	3 917(3)	7 031(6)	2 636(2)	C(29)	3 599(2)	208(5)	2 145(2)
C(15)	4 044(2)	6 317(5)	2 205(2)	C(30)	3 850(2)	1 375(5)	2 032(2)
C(16)	4 541(3)	6 594(7)	1 921(3)	C(31)	4 224(2)	2 215(6)	2 357(2)
N(1)	3 083(2)	3 282(4)	850(1)	B	3 170(2)	809(6)	813(2)

* Fractional coordinates × 10^5.

suitable crystals of the phenylphenoxide complexes for X-ray study were unsuccessful.

Fractional atomic coordinates are shown in Tables 1–3, the respective molecular structures of the complexes are illustrated in Figs. 1–3 and selected bond distances and angles are presented in Table 4.

Molecules of $[ZrL(OC_6H_4NO_2\text{-}4)_3]$ possess C_3 symmetry (Fig. 4) with the zirconium, boron and the hydrogen atom bonded to boron lying on a crystallographic three-fold axis. An approximation to C_{3v} symmetry is evident in that the three 4-nitrophenyl rings are twisted only slightly [4.3(2)°] out of the three putative mirror planes. The pseudo-octahedral co-ordination geometry at the zirconium atom shows significant trigonal distortion, although less so than in the case of $[Zr\{HB(pz)_3\}(\eta^5\text{-}C_5H_5)(OC_6H_4Ph\text{-}2)_2]$.[8] The ligand L appears to have a slightly larger 'bite angle' than that of $HB(pz)_3$, the three N–Zr–N angles in $[ZrL(OC_6H_4NO_2\text{-}4)_3]$ being 79.4(1)°, as compared to the mean of 76.1(1) in $[Zr\{HB(pz)_3\}(\eta^5\text{-}C_5H_5)(OC_6H_4Ph\text{-}2)_2]$.[8] The O–Zr–O angles are 98.6(1)°, approximately equal to the value of 99.2(2)° found in $[Zr\{HB(pz)_3\}(\eta^5\text{-}C_5H_5)(OC_6H_4Ph\text{-}2)_2]$.[8] The *cis*-N–Zr–O angles are close to 90° while the *trans*-N–Zr–O angles are 166.4(1)°. The large Zr–O–C angles are noteworthy and are consistent with a considerable degree of p_π–d_π electron donation from the ligands to the metal. The zirconium in $[ZrL(OC_6H_4NO_2\text{-}4)_3]$ is formally a twelve-electron centre and is thus highly electron deficient. In contrast, the zirconium atom in the complex $[Zr\{HB(pz)_3\}(\eta^5\text{-}C_5H_5)(OC_6H_4Ph\text{-}2)_2]$ is formally a sixteen-electron centre so that, whilst it might be expected to participate in some p_π–d_π dative electron bonding from the ligand to the metal, it is less electron

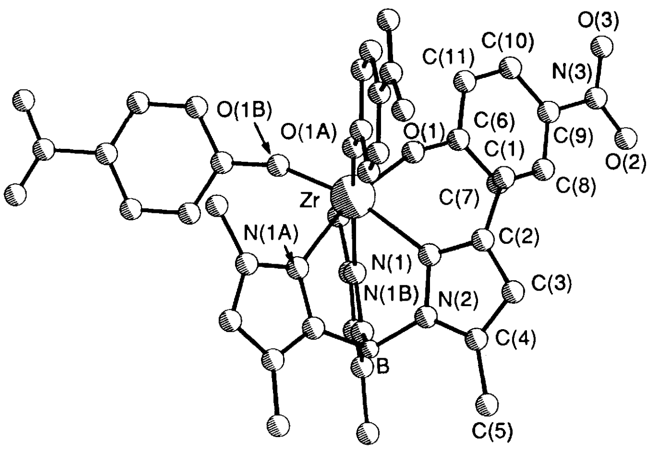


Fig. 1 The molecular structure of $[ZrL(OC_6H_4NO_2\text{-}4)_3]$ **1** showing the atom numbering. Hydrogen atoms have been omitted for clarity

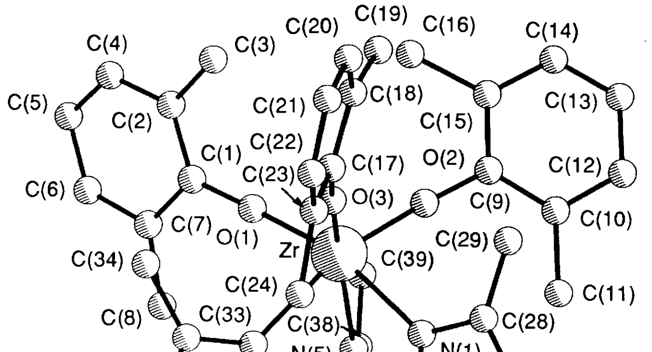


Fig. 2 The molecular structure of $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$ **2** showing the atom numbering. Hydrogen atoms have been omitted for clarity

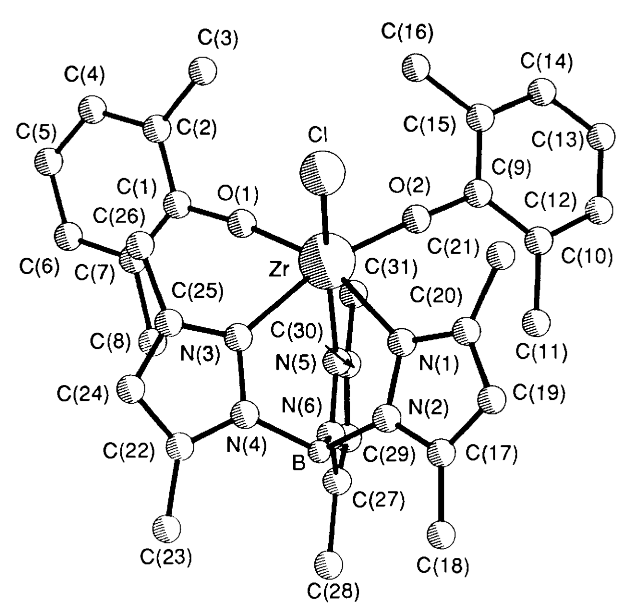


Fig. 3 The molecular structure of $[ZrL(Cl)(OC_6H_3Me_2\text{-}2,6)_2]$ **3** showing the atom numbering. Hydrogen atoms have been omitted for clarity

deficient than the metal centre in $[ZrL(OC_6H_4NO_2\text{-}4)_3]$. This may partly explain the relative bond angles at the oxygen atoms in these molecules, 146.5° (mean) in the former and 161.4(1)° in the latter. The Zr–O bond lengths also reflect this phenomenon, those in $[ZrL(OC_6H_4NO_2\text{-}4)_3]$ being 1.978(1) Å, shorter than those of 2.015(4) and 1.987(5) Å of $[Zr\{HB(pz)_3\}(\eta^5\text{-}C_5H_5)(OC_6H_4Ph\text{-}2)_2]$.[8] Thus, there appears to be a greater degree of multiple bonding between zirconium and oxygen in $[ZrL(OC_6H_4NO_2\text{-}4)_3]$. There are no intermolecular contacts which might affect the geometry of this complex.

The tris(phenoxide) derivative $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$, which contains the more sterically bulky 2,6-dimethylphenoxide ligand, also has approximate C_3 symmetry (Fig. 4), with packing forces producing slight divergences of the lengths and angles of otherwise chemically identical fragments. The molecule has Zr–N bond lengths ranging from 2.327(4) to 2.342(4) Å, and N–Zr–N angles ranging from 77.8(2) to 79.4(1)°. Overall the mean Zr–N length is slightly larger and the mean N–Zr–N angle smaller than those in $[ZrL(OC_6H_4NO_2\text{-}4)_3]$. The O–Zr–O angles are in the range 100.4(1)–102.0(2)°, and the Zr–O bond lengths, averaging 1.973 Å, are just shorter than the 1.978(1) Å found in $[ZrL(OC_6H_4NO_2\text{-}4)_3]$. The implication that there may be significant p_π–d_π donation from the oxygen to zirconium is supported by the remarkably large angles at the oxygen atoms, averaging 175.1°. The *cis*-N–Zr–O angles average 89.2° and the *trans*-angle mean is 163.5°.

The degree of distortion from a perfect octahedron is a little less in the closely related complex $[ZrLCl(OC_6H_3Me_2\text{-}2,6)_2]$, which is less sterically crowded (Figs. 3 and 4). In this structure the Zr–N lengths are a little shorter than in $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$, ranging from 2.289(4) to 2.334(4) Å. The Zr–N(pyrazolyl) bond *trans* to the halogen is the shortest of the Zr–N bonds in this structure and is, in fact, the shortest Zr–N bond in the three structures. A similar phenomenon has been noted previously[14] for structures containing the $Mo(NO)L(X)^+$ (X = Cl or I) moiety, and is presumably due to metal–halogen bonds involving little or no π interactions and thus exerting little or no *trans* influence. The N–Zr–N angles range from 76.9(1) to 82.3(1)°, the mean being a little larger than that in $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$. Interestingly, the mean Zr–O distance of 1.948 Å is also slightly shorter in $[ZrL(Cl)(OC_6H_3Me_2\text{-}2,6)_2]$ than in $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$. Bearing in mind the loose inverse relationship between Zr–O bond length and angle at the oxygen,[13] the structure of $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$ is atypical having both longer bond distances and a marginally greater mean oxygen angle than for $[ZrL(Cl)(OC_6H_3Me_2\text{-}2,6)_2]$. It is probable that steric as well as electronic effects play a role in determining the bonding geometry in these compounds. The more sterically crowded $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$ has the longer bond lengths and larger angles due to interactions between tightly packed ligands. The *cis*-N–Zr–O angles average 89.3° and the *trans* angles average 164.4°.

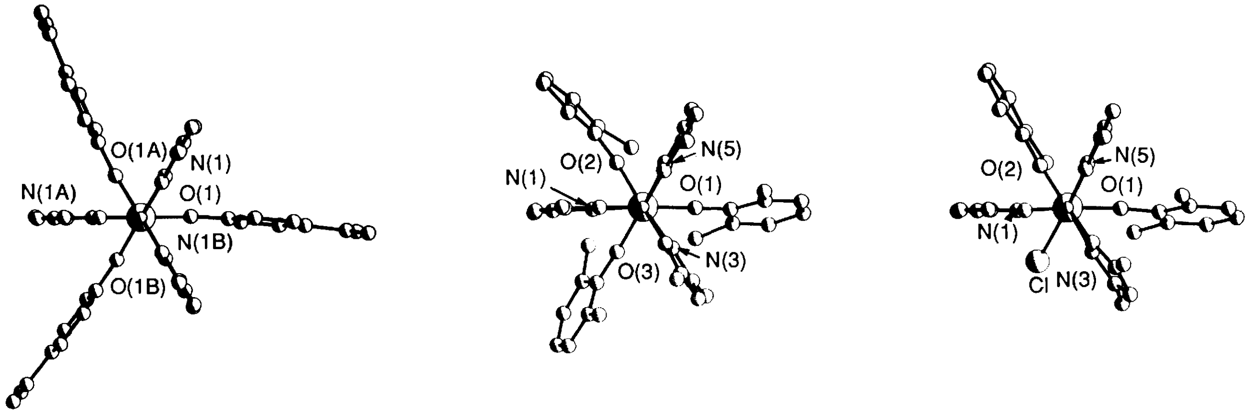
Comparing the three structures it can be seen from Fig. 4 that the phenyl rings in $[ZrL(OC_6H_4NO_2\text{-}4)_3]$ essentially lie in the plane bisecting the two adjacent pyrazolyl groups of the ligand L. In the case of $[ZrL(Cl)(OC_6H_3Me_2\text{-}2,6)_2]$ one of the two phenyl rings is twisted significantly out of this plane whilst in $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$ all three phenyl rings twist out of this plane.

As far as the co-ordination geometry at zirconium is concerned, there is a trend upon going from the less to the more sterically crowded complexes. Thus the mean deviation of angles at Zr from the ideal octahedral values of 90 or 180° is 6.6° in $[ZrL(OC_6H_4NO_2\text{-}4)_3]$, 8.0° in $[ZrL(Cl)(OC_6H_3Me_2\text{-}2,6)_2]$ and 8.8° in $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$. In the complex $[ZrL(OBu^t)Me(MeC{=}NBu^t)]$[12] which is highly sterically crowded the mean angular deviation from ideal octahedral is even greater, with a mean deviation of 10.9° for the 10 angles at

Table 4 Selected bond lengths (Å) and angles (°)

	$[ZrL(OC_6H_4NO_2\text{-}4)_3]$	$[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$	$[ZrL(Cl)(OC_6H_3Me_2\text{-}2,6)_2]$
Zr–O(1)	1.978(1)[a]	1.973(4)	1.949(3)
Zr–O(2)	1.978(1)	1.978(4)	1.948(3)
Zr–O(3)	1.978(1)	1.967(3)	2.439(1)[b]
Zr–N(1)	2.300(2)	2.327(4)	2.317(4)
Zr–N(3)	2.300(2)	2.342(4)	2.334(4)
Zr–N(5)	2.300(2)	2.333(5)	2.289(4)
O(1)–Zr–O(2)	98.6(1)	100.4(1)	104.7(1)
O(1)–Zr–O(3)	98.6(1)	100.6(2)	100.0(1)
O(2)–Zr–O(3)	98.6(1)	102.0(2)	96.9(1)
O(1)–Zr–N(1)	166.4(1)	165.8(1)	159.9(1)
O(2)–Zr–N(1)	90.0(1)	90.7(2)	90.7(1)
O(3)–Zr–N(1)	90.4(1)	85.6(2)	90.7(1)
O(1)–Zr–N(3)	90.4(1)	87.7(2)	86.0(1)
O(2)–Zr–N(3)	166.4(1)	163.4(1)	165.6(1)
O(3)–Zr–N(3)	90.0(1)	90.6(2)	90.5(1)
O(1)–Zr–N(5)	90.0(1)	93.7(2)	89.6(1)
O(2)–Zr–N(5)	90.4(1)	87.1(2)	88.1(1)
O(3)–Zr–N(5)	166.4(1)	161.3(1)	167.6(1)
N(1)–Zr–N(3)	79.4(1)	79.4(1)	76.9(1)
N(1)–Zr–N(5)	79.4(1)	78.0(2)	77.8(1)
N(3)–Zr–N(5)	79.4(1)	77.8(2)	82.3(1)
Zr–O(1)–C	161.4(1)	176.8(4)	172.3(3)
Zr–O(2)–C	161.4(1)	173.5(4)	176.8(3)
Zr–O(3)–C	161.4(1)	174.9(3)	—

[a] For $[ZrL(OC_6H_4NO_2\text{-}4)_3]$, O(2), O(3) refer to equivalent positions *z,x,y*; *y,z,x*, respectively, and N(1), N(3), N(5) refer to the positions *z,x,y*; *y,z,x*; *x,y,z*, respectively, with respect to the coordinates listed for O(1) and N(1) in Table 1. [b] For $[ZrL(Cl)(OC_6H_3Me_2\text{-}2,6)_2]$, O(3) refers to the chlorine atom.



1 2 3

Fig. 4 The molecular structures of compounds **1**–**3** viewed along the B–Zr axis and showing the orientation of the phenyl rings with respect to the planes defined by the pyrazolyl rings of the tris(dimethylpyrazolyl)borate ligand

zirconium excluding those involving the iminoacyl ligand. When the structure of this complex was reported the bond angle at oxygen of 174.3(5)° was the largest known Zr–O–C angle. This appears to have been superseded by angles of 176.8° in both $[ZrL(OC_6H_3Me_2\text{-}2,6)_3]$ and $[ZrL(Cl)(OC_6H_3Me_2\text{-}2,6)_2]$.

Experimental

Synthetic Studies.—All reactions were performed under an atmosphere of dry nitrogen, but products were treated as air-stable. Solvents used for these reactions were purified by distillation from standard drying agents under dry nitrogen. Solvents were used as supplied for air-stable compounds, with the exception of tetrahydrofuran which was distilled prior to use. Triethylamine was dried by distillation from phosphorus pentaoxide before use. Other reagents were used as supplied, with only preliminary drying *in vacuo* for a few minutes. The salt $K[HB(3,5\text{-}Me_2C_3N_2H)_3]$ (KL)[15] and $[ZrLCl_3]$[10] were prepared according to reported methods.

Elemental analyses were performed by the Microanalytical Laboratory of the University of Birmingham. Infrared and mass spectra were recorded on PE 297 and Kratos MS80RF instruments respectively and ^1H NMR spectra using PE R12B (60 MHz) and JEOL GX270 (270 MHz) instruments.

General Preparation of Crude $[ZrL(OC_6H_4Z)_3]$ (Z = H, 2-, 3-, or 4-F, 3- or 4-NO_2, or 4-Bu^t).—The compound $[ZrLCl_3]$ (0.4 g, 0.81 mmol) was mixed with 3 mol equivalents of the appropriate phenol in a Schlenk tube containing a magnetic follower. Dry CH_2Cl_2 (50 cm^3) was added *via* a cannula and the mixture stirred until dissolution was complete. Three mol equivalents of NEt_3 were added by syringe and the mixture stirred for 15 min. All volatile materials were then removed under reduced pressure and the resulting solid extracted with tetrahydrofuran (thf) (2 × 20 cm^3) in air. The extract was filtered then evaporated under reduced pressure to give an oil which was redissolved in CH_2Cl_2–hexane to give a solution from which the crude product was deposited upon partial evaporation.

Purification Procedures.—$[ZrL(OPh)_3]$ (*crude yield* 0.184 g, 88%). The crude solid was heated to 180 °C *in vacuo* for a few minutes, cooled and dissolved in CH_2Cl_2 (10 cm^3). Pentane was added until the solution just became turbid; it was centrifuged to remove the precipitate and more dichloromethane (10 cm^3) and hexane (2 cm^3) added. The purified material deposited as colourless needles on standing, m.p. 248 °C (Found: C, 59.3; H, 5.5; N, 12.7%; M^+ 666. $C_{33}H_{37}BN_6O_3Zr$ requires C, 59.4; H, 5.4; N, 12.6%; M_r 667.7). $\delta_H(CDCl_3)$ 6.66, 6.76, 7.09 (6 H, d, 3 H, t, 6 H, t, C_6H_5], 5.71 (3 H, s, $C_3\mathit{H}N_2Me_2$), 2.44 and 2.11 [9 H, s, 9 H, s, $C_3HN_2(C\mathit{H}_3)_2$]. *m/z* (EI) 666 (*M*), 573 (*M* − OPh) and 375 $[Zr(3,5\text{-}Me_2C_3N_2H)_3]$.

$[ZrL(OC_6H_4NO_2\text{-}3)_3]$ (*crude yield* 0.359 g, 74%). The crude solid was heated to 180 °C *in vacuo* for a few minutes, cooled and dissolved in CH_2Cl_2 (20 cm^3). Toluene was added until the solution just became turbid, it was then centrifuged and the clear supernatant evaporated under reduced pressure until a brown impurity was deposited. After further centrifugation, the supernatant was evaporated further and deposited a cream coloured solid which was collected, washed in toluene (2 cm^3) and dried. This procedure was repeated to give the purified product as a straw coloured powder, m.p. 213–216 °C (Found: C, 49.6; H, 4.2; N, 15.7%; M^+ 801. $C_{33}H_{34}BN_9O_9Zr$ requires C, 49.4; H, 4.3; N, 15.7%; M_r 802.7). $\delta_H(CDCl_3)$ 7.68, 7.26, 6.95 (3 H, d, 6 H, t, 3 H, d, C_6H_4), 5.77 (3 H, s, $C_3\mathit{H}N_2Me_2$), 2.17 and 2.03 [9 H, s, 9 H, s, $C_3HN_2(C\mathit{H}_3)_2$]. *m/z* (EI) 801 (*M*), 663 (*M* − $OC_6H_4NO_2$) and 375 $[Zr(3,5\text{-}Me_2C_3N_2H)_3]$.

$[ZrL(OC_6H_4NO_2\text{-}4)_3]$ (*crude yield* 0.580 g, 78%). The crude oil was dissolved in CH_2Cl_2 (20 cm^3). Pentane was added until the solution just became turbid; it was centrifuged to remove the precipitate and more dichloromethane (10 cm^3) and hexane (4 cm^3) added. Straw coloured crystals were deposited after standing overnight in air, m.p. 290–300 °C (Found: C, 49.1; H, 4.4; N, 16.0%; M^+ 801. $C_{33}H_{34}BN_9O_9Zr$ requires C, 49.4; H, 4.3; N, 15.7%; M_r 802.7). $\delta_H(CDCl_3)$ 8.05, 6.59 (6 H, d, 6 H, d, C_6H_4), 5.80 (3 H, s, $C_3\mathit{H}N_2Me_2$), 2.51 and 2.01 [9 H, s, 9 H, s, $C_3HN_2(C\mathit{H}_3)_2$]. *m/z* (EI) 801 (*M*), 663 (*M* − $OC_6H_4NO_2$) and 375 $[Zr(3,5\text{-}Me_2C_3N_2H)_3]$.

$[ZrL(OC_6H_4F\text{-}2)_3]$ (*crude yield* 0.560 g, 88%). The crude solid was dissolved in CH_2Cl_2 (30 cm^3). Hexane was added until the solution just became turbid; it was centrifuged to remove the precipitate and more pentane (5 cm^3) and hexane (5 cm^3) added. The purified material deposited as colourless needles on standing overnight, m.p. 251–253 °C (Found: C, 54.7; H, 4.5; N, 11.7%; M^+ 720. $C_{33}H_{34}BF_3N_6O_3Zr$ requires C, 54.9; H, 4.7; N, 11.6%; M_r 721.7). $\delta_H(CDCl_3)$ 6.82 (12 H, m, C_6H_4), 5.71 (3 H, s, $C_3\mathit{H}N_2Me_2$), 2.43 and 2.11 [9 H, s, 9 H, s, $C_3HN_2(C\mathit{H}_3)_2$]. *m/z* (EI) 720 (*M*), 609 (*M* − OC_6H_4F) and 375 $[Zr(3,5\text{-}Me_2C_3N_2H)_3]$.

$[ZrL(OC_6H_4F\text{-}3)_3]$ (*crude yield* 0.452 g, 51%). The crude solid was dissolved in thf (10 cm^3) and the solution evaporated to *ca.* 2 cm^3. Hexane (30 cm^3) was then added and the resulting suspension allowed to settle. The supernatant deposited fine white crystals on standing and these were recrystallised from CH_2Cl_2–pentane–hexane (20 cm^3–5 cm^3–5 cm^3), m.p. 224–226 °C (Found: C, 55.0; H, 4.8; N, 11.8%; M^+ 720. $C_{33}H_{34}BF_3N_6O_3Zr$ requires C, 54.9; H, 4.7; N, 11.6%; M_r 721.7). $\delta_H(CDCl_3)$ 7.02, 6.46, 6.27 (3 H, m, 6 H, m, 3 H, d, C_6H_4), 5.74 (3 H, s, $C_3\mathit{H}N_2Me_2$), 2.46 and 2.10 [9 H, s, 9 H, s, $C_3HN_2(C\mathit{H}_3)_2$]. *m/z* (EI) 720 (*M*), 609 (*M* − OC_6H_4F) and 375 $[Zr(3,5\text{-}Me_2C_3N_2H)_3]$.

$[ZrL(OC_6H_4F\text{-}4)_3]$ (*crude yield* 0.879 g, 86%). The crude solid was recrystallised from CH_2Cl_2–toluene (20 cm^3–20 cm^3) to give the product as pale pink crystals, m.p. 236 °C (Found: C, 55.1; H, 4.6; N, 11.6%; M^+ 720. $C_{33}H_{34}BF_3N_6O_3Zr$ requires C, 54.9; H, 4.7; N, 11.6%; M_r 721.7). $\delta_H(CDCl_3)$ 6.76, 6.51 (6 H, t, 6 H, m, C_6H_4), 5.72 (3 H, s, $C_3\mathit{H}N_2Me_2$), 2.45 and 2.08 [9 H, s, 9 H, s, $C_3HN_2(C\mathit{H}_3)_2$]. *m/z* (EI) 720 (*M*), 609 (*M* − OC_6H_4F) and 375 $[Zr(3,5\text{-}Me_2C_3N_2H)_3]$.

$[ZrL(OC_6H_4Bu^t\text{-}4)_3]$ (*crude yield* 0.221 g, 30%). The crude solid was dissolved in thf (40 cm^3) and the solution evaporated to *ca.* 2 cm^3. Hexane was added until a precipitate formed. This was removed by centrifugation and the supernatant evaporated to give an oil which was redissolved in dichloromethane–hexane (10 cm^3–2 cm^3). On standing overnight the solution deposited an oil containing some large crystals. The crystals were washed with the minimum amount of pentane to remove the oil, m.p. 213 °C (Found: C, 65.0; H, 7.4; N, 9.9%; M^+ 834. $C_{45}H_{61}BN_6O_3Zr$ requires C, 64.6; H, 7.4; N, 10.1%; M_r 836.0). $\delta_H(CDCl_3)$ 7.09, 6.61 (6 H, d, 6 H, d, C_6H_4), 5.70 (3 H, s, $C_3\mathit{H}N_2Me_2$), 2.43, 2.14 [9 H, s, 9 H, s, $C_3HN_2(C\mathit{H}_3)_2$] and 1.24 [9 H, s, $C(CH_3)_3$]. *m/z* (EI) 834 (*M*), 685 (*M* − $OC_6H_4CMe_3$) and 375 $[Zr(3,5\text{-}Me_2C_3N_2H)_3]$.

$[ZrL(Cl)(OC_6H_4Ph\text{-}2)_2]$. The compound $[ZrLCl_3]$ (0.360 g, 0.726 mmol) was dissolved in dry CH_2Cl_2 (100 cm^3) and a solution of 2-phenylphenol (0.251 g, 1.48 mmol) in CH_2Cl_2 (100 cm^3) was added dropwise, with stirring, over 30 min. The solution was heated under reflux for 10 min and the solvent removed under reduced pressure. The residue was extracted with thf (2 × 10 cm^3) and the combined extracts evaporated to dryness, redissolved in CH_2Cl_2–hexane (50 cm^3–15 cm^3) and set aside to evaporate slowly. A precipitate deposited and was removed by periodic centrifugation. After *ca.* 5 d the white product began to deposit on the walls of the flask and when only *ca.* 1 cm^3 of solution remained the solid was collected and washed with diethyl ether (2 × 10 cm^3) (crude yield 0.244 g, 44%). This material was dissolved in toluene (10 cm^3), concentrated to 2 cm^3, and stored at −20 °C overnight to give a white solid which was further recrystallised from CH_2Cl_2–cyclohexane, m.p. 255 °C (Found: C, 61.1; H, 5.0; N, 11.2%; M^+ 760. $C_{39}H_{40}BClN_6O_2Zr$ requires C, 61.4; H, 5.3; N, 11.0%; M_r 762.3). $\delta_H(CDCl_3)$ 7.25, 7.05, 6.87, 6.19 (3 H, m, 8 H, m, 5 H, m, 2 H, d, $C_6H_4C_6H_5$), 5.65, 5.49 (2 H, s, 1 H, s, $C_3\mathit{H}N_2Me_2$), 2.46, 2.42, 2.24 and 1.62 [3 H, s, 6 H, s, 6 H, s, 3 H, s, $C_3HN_2(C\mathit{H}_3)_2$]. *m/z* (EI) 760 (*M*), 725 (*M* − Cl), 591 (*M* − OC_6H_4Ph), 449 $[Zr(OC_6H_4Ph)(3,5\text{-}Me_2C_3N_2H)_2]$ and 375 $[Zr(3,5\text{-}Me_2C_3N_2H)_3]$.

$[ZrL(OC_6H_4Ph\text{-}2)_3]$. The compound $[ZrLCl_3]$ (131 mg, 0.264 mmol) and 2-phenylphenol (136 mg, 0.799 mmol) were stirred in CH_2Cl_2 (60 cm^3) until complete dissolution had occurred. Dry NEt_3 (0.2 cm^3, 1.5 mmol) was then added by syringe. After stirring the mixture for 10 min the volatile materials were removed *in vacuo*. The residue was extracted with diethyl ether (60 cm^3) and thf (2 × 20 cm^3), and the combined extracts evaporated under reduced pressure to give an oil. This was redissolved in diethyl ether (30 cm^3) and the solution left to stand overnight to deposit the white product (crude yield 137 mg, 58%). This was recrystallised from CH_2Cl_2–cyclohexane (20 cm^3–5 cm^3) to afford the white product, which was washed with cyclohexane (5 cm^3) and dried *in vacuo*, m.p. 279 °C (Found: C, 68.4; H, 5.6; N, 9.5%; M^+ 894. $C_{51}H_{49}BN_6O_3Zr$ requires C, 68.4; H, 5.5; N, 9.4%; M_r 896.0). $\delta_H(CDCl_3)$ 7.20, 7.03, 6.85, 6.14 (5 H, m, 5 H, m, 13 H, m, 4 H, m, $C_6H_4C_6H_5$), 5.46 (3 H, s, $C_3\mathit{H}N_2Me_2$), 2.47 and 1.69 [9 H, s, 9 H, s, $C_3HN_2(C\mathit{H}_3)_2$]. *m/z* (EI) 894 (*M*), 725 (*M* − OC_6H_4Ph), 449 $[Zr(OC_6H_4Ph)(3,5\text{-}Me_2C_3N_2H)_2]$ and 375 $[Zr(3,5\text{-}Me_2C_3N_2H)_3]$.

$[ZrLCl_2(OC_6H_3Me_2\text{-}2,6)]$. The compound $[ZrLCl_3]$ (46 mg, 0.093 mmol) and 2,6-dimethylphenol (24 mg, 0.194 mmol) were dissolved in dry toluene (100 cm^3) heated under reflux for 24 h. After this time the solvent was removed under reduced pressure and the residue treated with CH_2Cl_2–toluene (5 cm^3–5 cm^3) to afford a suspension. After settling the supernatant was removed using a cannula. The solid residue was dissolved in CH_2Cl_2 (20 cm^3), filtered and cyclohexane (10 cm^3) was added to the filtrate. The solution thus obtained was then concentrated under reduced pressure to give a solid which was collected and washed with diethyl ether (3 cm^3). The solid was heated to *ca.* 180 °C *in vacuo* in order to remove volatile materials and recrystallised from CH_2Cl_2–cyclohexane (3 cm^3–1 cm^3) to give straw coloured needles (crude yield 35 mg, 65%). Further purification was effected by recrystallisation from CH_2Cl_2–hexane–cyclohexane (1 cm^3 of each), m.p. 284 °C (Found: C, 48.7; H, 5.5; N, 14.6%; M^+ 579. $C_{23}H_{31}BCl_2N_6OZr$ requires C, 47.6; H, 5.5; N, 14.9%; M_r 580.5). $\delta_H(CDCl_3)$ 7.02, 6.80, 6.75 (1 H, d, 1 H, d, 1 H, t, C_6H_4), 5.86, 5.77 (1 H, s, 2 H, s, $C_3\mathit{H}N_2Me_2$), 2.79, 2.77, 2.41, 2.30 and 1.45 [3 H, s, 3 H, s, 9 H, s, 6 H, s, 3 H, s, $C_3HN_2(C\mathit{H}_3)_2$, $C_6H_3(C\mathit{H}_3)_2$]. *m/z* (EI) 579 (*M*), 458 (*M* − $OC_6H_3Me_2$) and 375 [Zr(3,5-$Me_2C_3N_2H)_3$].

[ZrL(Cl)($OC_6H_3Me_2$-2,6$)_2$]. The compound [$ZrLCl_3$] (605 mg, 1.22 mmol) and 2,6-dimethylphenol (476 mg, 3.90 mmol) were dissolved in dry xylene (100 cm^3) and heated under reflux for 1 week. After this time the solvent was removed under reduced pressure, the brown residue dispersed in CH_2Cl_2 (5 cm^3) and the mixture centrifuged. Dichloromethane (2 cm^3) and cyclohexane (2 cm^3) were added to the supernatant and the mixture left to stand for 4 h. During this time more material precipitated and was removed by centrifugation. The solvent was removed from the supernatant under reduced pressure and hexane (20 cm^3) and dichloromethane (10 cm^3) added. On standing the solution deposited a cream solid which was collected and washed with hexane (3 cm^3) then recrystallised from CH_2Cl_2–cyclohexane (crude yield 0.122 g, 22%). Further purification was effected by recrystallisation from dichloromethane–toluene (2 cm^3–2 cm^3), m.p. 358 °C (Found: C, 57.1; H, 6.3; N, 12.3%; M^+ 664. $C_{31}H_{40}BClN_6O_2Zr$ requires C, 55.9; H, 6.1; N, 12.6%; M_r 666.2). $\delta_H(CDCl_3)$ 6.96, 6.73, 6.66 (3 H, d, 3 H, d, 3 H, t, C_6H_3), 5.72 (3 H, s, $C_3\mathit{H}N_2Me_2$), 2.71, 2.45, 2.40, 2.25, 2.10 and 1.23 [6 H, s, 3 H, s, 6 H, s, 6 H, s, 3 H, s, 6 H, $C_3HN_2(C\mathit{H}_3)_2$, $C_6H_3(C\mathit{H}_3)_2$]. *m/z* (EI) 664 (*M*), 629 (*M* − Cl), 401 [Zr($OC_6H_3Me_2$)(3,5-$Me_2C_3N_2H)_2$] and 375 [Zr(3,5-$Me_2C_3N_2H)_3$].

[ZrL($OC_6H_3Me_2$-2,6$)_3$]. The compound [$ZrLCl_3$] (80 mg, 0.163 mmol) and 2,6-dimethylphenol (60 mg, 0.494 mmol) were dissolved in CH_2Cl_2 (60 cm^3) and NEt_3 (230 μl, 1.66 mmol) added. The solution was heated under reflux for 10 min then left to stand for 30 min after which time the solvent was removed under reduced pressure. The residue was heated to 180 °C *in vacuo* to remove volatile materials and the resulting solid extracted with tetrahydrofuran (2 × 20 cm^3). The extracts were evaporated to dryness and the residue redissolved in CH_2Cl_2 (20 cm^3). Hexane (5 cm^3) was added and the mixture left to evaporate slowly. After 3 d the amber crystals which formed were collected and washed with hexane (3 cm^3), dichloromethane–hexane (1:10, 3 cm^3) and hexane (1 cm^3) (crude yield 36 mg, 30%). Further purification was effected by recrystallisation from CH_2Cl_2–toluene–diethyl ether solution (50 cm^3–5 cm^3–10 cm^3), decomp. <355 °C (Found: C, 62.1; H, 6.8; N, 11.5%; M^+ 750. $C_{39}H_{49}BN_6O_3Zr$ requires C, 62.3; H, 6.6; N, 11.2%; M_r 751.9). $\delta_H(CDCl_3)$ 6.93, 6.73, 6.60 (3 H, d, 3 H, d, 3 H, t, C_6H_3), 5.64 (3 H, s, $C_3\mathit{H}N_2Me_2$), 2.59, 2.43, 1.89 and 1.23 [9 H, s, 9 H, s, 9 H, s, 9 H, s, $C_3HN_2(C\mathit{H}_3)_2$, $C_6H_3(C\mathit{H}_3)_2$]. *m/z* (EI) 750 (*M*) 629 (*M* − $OC_6H_3Me_2$), 401 [Zr($OC_6H_3Me_2$)(3,5-$Me_2C_3N_2H)_2$] and 375 [Zr(3,5-$Me_2C_3N_2H)_3$].

[$ZrLCl_2$($OC_6H_3Ph_2$-2,6)]. The use of dry solvents is essential for the success of this reaction. The compound [$ZrLCl_3$] (176 mg, 0.355 mmol) and 2,6-dimethylphenol (261 mg, 1.061 mmol) were dissolved in CH_2Cl_2 (105 cm^3) and the solution stirred for 2 h. After this time NEt_3 (145 μl, 1.05 mmol) was added and the mixture heated under reflux for 5 min then allowed to stand for 2 h. The solvent was removed under reduced pressure, toluene (10 cm^3) added and the resulting suspension filtered. The solvent was then removed under reduced pressure, thf (10 cm^3) added and the resulting suspension filtered under dinitrogen. The solvent was again removed under reduced pressure and CH_2Cl_2 (10 cm^3) added to the residue. The resulting suspension was left overnight to settle, filtered under dinitrogen and the filtrate evaporated under reduced pressure. The residue was treated with CH_2Cl_2 (3 cm^3) and hexane (3 cm^3) and the resulting solution allowed to evaporate slowly under a stream of dinitrogen. After 3 d a precipitate of [$NHEt_3$]Cl was removed. The white microcrystalline product was obtained on further standing, washed with CH_2Cl_2–hexane (1:1, 4 cm^3) and dried (42 mg, 16%), m.p. 306 °C (Found: C, 54.3; H, 5.2; N, 11.0%; M^+ 703. $C_{33}H_{35}BCl_2N_6OZr\cdot 0.5CH_2Cl_2$ requires C, 53.9; H, 4.9; N, 11.2%; M_r 704.6). $\delta_H(CDCl_3)$ 7.73–6.55 (13 H, $C_6\mathit{H}_3C_6\mathit{H}_5$) 5.69, 5.53 (1 H, s, 2 H, s, $C_3\mathit{H}N_2Me_2$), 2.53, 2.37, 2.28 and 2.21 [3 H, s, 6 H, s, 3 H, s, 6 H, s, $C_3HN_2(C\mathit{H}_3)_2$]. *m/z* (EI) 801 (*M*) and 458 (*M* − $OC_6H_3Ph_2$).

Structural Studies.—Crystal data. [ZrL($OC_6H_4NO_2$-4$)_3$] **1**, M_r = 802.7, trigonal, space group $R\bar{3}$ (no. 148), a = 12.211(3) Å, α = 93.85(4)°, U = 1807.9 $Å^3$, Z = 2, D_c = 1.475 g cm^{-3}, $F(000)$ = 824, μ(Mo-Kα) = 0.361 mm^{-1}. [ZrL($OC_6H_3Me_2$-2,6$)_3$] **2**, M_r = 751.9, monoclinic, space group Cc (no. 9), a = 20.23(2), b = 10.663(8), c = 18.590(6) Å, β = 107.0(1)°, U = 3835 $Å^3$, Z = 4, D_c = 1.302 g cm^{-3}, $F(000)$ = 1576, μ(Mo-Kα) = 0.323 mm^{-1}. [ZrL(Cl)($OC_6H_3Me_2$-2,6$)_2$] **3**, M_r = 666.2, monoclinic, space group $C2/c$ (no. 15), a = 24.449(5), b = 10.180(8), c = 26.79(2) Å, β = 92.15(2)°, U = 6663 $Å^3$, Z = 8, D_c = 1.328 g cm^{-3}, $F(000)$ = 2768, μ(Mo-Kα) = 0.438 mm^{-1}.

Cell dimensions and intensity data were measured with an Enraf-Nonius CAD-4 diffractometer operating in the ω–2θ scan mode using Mo-Kα radiation. Angular ranges for data collection were θ = 2–24° for compound **1** and 2–25° for **2** and **3**. 1767 Reflections for **1**, 3821 for **2** and 3178 for **3** having $I > 2.5\sigma(I)$ were used in the analyses. Three standard reflections were measured every 2 h to check the stability of the system. The structure of compound **1** was determined by direct methods[16] and those of **2** and **3** by Patterson and Fourier methods.[16] Refinement[17] was by least squares. Non-hydrogen atoms were allowed to vibrate anisotropically. Hydrogen atoms were included in calculated positions riding on their respective carbon atoms so that the methyl hydrogens are staggered with respect to other atoms bonded to the adjacent carbon atom. Isotropic thermal parameters were refined (**1**) and fixed at U = 0.1 (**2**) and 0.07 $Å^2$ (**3**). The calculations were terminated when all calculated shifts were <0.1σ and R, R' were 0.027, 0.038 for **1**, 0.030, 0.039 for **2** and 0.044, 0.060 for **3**. The weighting schemes were $w = 1/\sigma^2(F)$ for **1** and $1/[\sigma^2(F) + 0.0004F^2]$ for **2** and **3**. The residual electron density in the final difference map was within the range ±0.5 e $Å^{-3}$ for all three structures. Figures were drawn with PLUTO.[18]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We are grateful to the SERC and to BP Chemicals for financial support (to R. A. K.) under the C.A.S.E. scheme.

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Received 5th November 1990; *Paper* 0/04977H